

Comments on "The rotational isomers of the monohalogeno-substituted derivatives of n-pentane and n-octane"*

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IN an earlier paper [1] we were able to show that in secondary alkyl chlorides the absorption bands arising primarily from the stretching of the carbon-chlorine bond fall in non-overlapping frequency ranges which depend both on the two atoms *trans* to the chlorine atom across the neighboring carbon-carbon bonds and on the local conformation of the carbon chain. These correlations were based on the study of many model compounds, several having unique conformations, and represented a more detailed extension of previous observations [2].

GATES *et al.* [3] now assert that the nomenclature which we used for describing rotational isomers is "insufficient" and that some of our assignments "need modification." Both of these claims are erroneous. Furthermore, their proposed modifications in assignments are incorrect.

To begin with, despite the statements made by these authors (p. 2045 of Ref. [3]), a casual reading of our paper (pages 1607 and 1610 of Ref. [1]) shows that we did indeed consider both bent forms in which chlorine is *trans* to two hydrogens, and that our nomenclature (S''_{HH} and S'_{HH}) can "allow" quite well for their description. Nor is it true that we "only considered four possible conformations for a general secondary isomer." We explicitly designated five of the six, viz., S_{HH} , S'_{HH} , S''_{HH} , S_{CH} , and S_{CC} . The sixth, S'_{OH} , was explicitly noted by CARACULACU *et al.* [4], who experienced no difficulty in the obvious extension of our nomenclature. The reason that we did not mention the S'_{OH} structure is that we were concerned with carbon-chlorine stretching frequencies, not "X-sensitive bands", and there was no evidence then, nor is there any now, that the S'_{OH} frequency range is spectroscopically distinguishable from the S_{OH} frequency range. In a similar vein, the distinction which we made between P_H and P'_H frequencies for primary chlorides (the latter corresponding to the case of a branch on the carbon atom α to the $-\text{CH}_2\text{Cl}$ group) is far from being "unnecessary"; it is decidedly useful, since the frequency ranges represented by these two kinds of structures do not overlap. This is most probably due, by analogy with the case of the secondary chlorides [5], to the different mass distributions around the C-Cl bond, not, as the above authors claim, to "molecular crowding."

In the notation of Gates *et al.* the two hydrogen atoms *trans* to the chlorine atom when the carbon backbone is in the planar zigzag form are designated H'. If these atoms had been designated by H, the other hydrogen of the methylene group being labeled H', then their notation would coincide with ours (except for the minor modification recently introduced [4, 5] of replacing S'_{HH} with S_{HH} , S''_{HH} with $S_{H'H}$, etc.). Thus, despite their claim, we did differentiate between the two hydrogens on a carbon atom (our prime notation is equivalent to such a separate designation). The inversion of our notation, when agreement with it depended only on the location of a prime, is deplorable, particularly since our nomenclature has come into widespread use [e.g., 4-9]. We consider the substitution of nomenclature suggested by Gates *et al.* to be irrelevant and unnecessary.

* P. N. GATES, E. F. MOONEY and H. A. WILLIS, *Spectrochim. Acta* **23A**, 2043 (1967).

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A more serious objection is their claim that some of our assignments need modification. A recent normal coordinate analysis of secondary chlorides [5] has not only shown that our assignments were correct, but indicates that the proposals of the above authors are wrong. Their assignment (p. 2051 of Ref. [3]) of a fourth "X-sensitive band" in the spectrum of 2-chlorobutane is misleading. There are many bands in the spectra of secondary alkyl halides which are sensitive to the halogen atom present. The point of our paper [1] is that the carbon-halogen stretching modes are a characteristically good diagnostic for conformational structure. Other modes of particular molecules may also be in this category, but they should not be confused with the correlations based on the stretching frequencies. Furthermore, the assignment of the low frequency "X-sensitive band" to a "cis X—H conformation" (a structure which, incidentally, we have been unable to reconstruct from their description) is shown by the normal coordinate analysis [5] to be incorrect: this band is quite satisfactorily correlated with a normal mode of the S_{HR} conformation, and has a temperature behavior [3,5] consistent with this assignment. Also, the low frequency band of 3-chloropentane can be adequately accounted for by standard conformations other than S_{CC} [10], so there is no need to postulate (p. 2053 of Ref. [3]) this bizarre departure from correlations which were established from molecules of unique conformation [1, 5]. The assignments suggested for 4-chloro-octane (pp. 2055, 2056 of Ref. [3]) are equally untenable.

We must conclude that the changes in nomenclature and correlations suggested by Gates, Mooney and Willis are without novelty or foundation, and that the nomenclature and correlations developed in our original paper [1] remain valid and useful.

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